09/937124
TO/PCT Rec'd 27 DEC 2001

F-7160

METHOD FOR CONTROLLING THE SIZE OF CRYSTALS DURING CONTINUOUS MASS CRYSTALLIZATION

During mass production by crystallization, the particle size must comply with strict specifications.

In order to minimize the manufacturing costs of such products, it is necessary to come as close as possible to these particle size distributions already during the crystallization process and to produce these distributions stably. The invention therefore relates to a method for controlling the size of crystals during a continuous mass crystallization.

Especially ammonium sulfate, as fertilizer or industrial product, is produced preferably by crystallization processes. For fertilizer production, a coarsely crystalline product with a defined particle size spectrum is demanded, in order to guarantee the required scatter and scatter accuracies. The industrial products should be of a finer crystalline size.

The mode of functioning and construction of a draft tube buffer crystallization apparatus (DTB crystallizer) are known (US patent 3,873,275)..

With this, the required particle size distributions can be produced, but cannot be produced stably. Because of their constructive design from the point of view of minimizing the formation of fine particles by the selective destruction of crystallization nuclei, the particle size distribution, especially of crystals produced in DTB crystallizers, has a great tendency to fluctuate cyclically.

An apparatus with a dynamic control method is also known. For this, various process variable, such as the rate of recycling the fine crystals, the flow of feed solution, the pH, the degree of mixing or the supply of seeding crystals is controlled on the basis of the analysis of the particle size distribution of the crystalline material in the crystallizing apparatus and, with that, a uniform particle size distribution is obtained (US patent 4,263,010).

However, this method is technologically very expensive and can hardly be designed stably.

A method for producing large crystals with a DTB crystallizer is also known. The offtake of crystals from the DTB crystallizer (production rate) varies depending on the determined density of the suspension in the crystallizing apparatus, the power consumption of the stirrer motor, the height of the crystalline bed under the baffle and the size distribution of the crystals (JP 150 127).

Admittedly, the proportion of crystals larger than 1.4 mm is increased. However, the proportion of crystals larger than 2.0 mm still fluctuates between 35% and 90%. The alternating, fluctuating production rate and, with that, the inadequate utilization of the installed capacity of the plant are extremely serious disadvantages for the downstream industrial units.

Furthermore, a method is known, by means of which the proportion of larger crystals in a DTB crystallizer is increased. For this method, a suspension of crystals with 6% to 25% by volume of crystals is supplied to the crystallizer, the solids of this suspension constituting 4% to 25% by weight of the solids withdrawn from the crystallizer. For this method, 35% to 85% by weight of the seeding crystals are larger than 1.2 mm and not more than 15% by weight of the crystals are larger than 1.7 mm (WO 93/19826).

The temperature of the seeding suspension is lower than the temperature of the crystallizer.

It is a disadvantage of the invention that only an averaging of the production and an increase in the proportion of larger crystals is achieved. Neither the selective control of the size of the crystals nor the production of a product with finer crystals is described or claimed.

It was therefore an object of the invention to eliminate these disadvantages, that is, to find a method for reproducibly controlling the size of the crystals during a continuous mass crystallization.

Pursuant to the invention, this is accomplished by a method, in which seeding products are added

- the seeding product, in its parameters, being produced independently of the actual crystallization process,
- the average particle diameter of the solids of the seeding products being 0.1 to 1.0 mm and smaller than that of the desired crystalline material,
- the solids of the seeding product being produced independently of the main process of crystallization from different industrial partial flows in the specified particle size region
- the temperature of the seeding product during the addition being as much as 40°C and preferably 10° to 30°C lower than the process temperature in the crystallizer and
- all other materials, fed and recycled into the crystallizer, being free solids.

A suspension of crystals, the parameters of which can be adjusted completely independently of the actual crystallization process, is supplied to the crystallization apparatus. This suspension is characterized by the solids content, by

the particle size distribution . and by the amount of product supplied to the crystallization apparatus in unit time.

The particle size distribution of the final product is affected by controlling the parameters of this seeding product and the fluctuations in the particle size distribution of the end product (solids taken off from the crystallization apparatus), are reduced.

The precise parameters of the seeding product for a given crystallization apparatus can be obtained empirically in relation to the desired, steady state of this apparatus.

This method can be carried out by adding the seeding product discontinuously as well as continuously.

When seeding discontinuously, the seeding product is added discontinuously in such a manner, that the proportion by weight of a selected fraction of the crystalline material in the crystallizer remains with in specified limits.

To prevent strong, cyclic fluctuations in the size of the crystals of the end product, an effective seed formation rate is required, which is adequate for the system, fluctuates slightly and is reflected in constant proportions over time of the individual fractions, particularly the fractions less than 1.0 mm. When the limiting range is not attained, seeding is carried out and, when the limiting range is exceeded, the seeding is suspended.

When seeding continuously, the proportion of solids of the seeding product is added in amounts of 5 to 30 percent by weight and preferably of 7 to 15 percent by weight, based on the solids, discharged, the crystallizer.

Advisably, the average particle diameter of the solids of the seeding product is 0.3 to 0.8 mm. In any case, it is less than the particle diameter of the desired, crystalline material.

The desired particle size of the solids of the seeding product can be adjusted by known procedures. Preferably, it is produced by a mechanical comminution of one of the fractions of the end product and/or in a separate stage of the crystallization. In other words, the end product is not used unchanged.

The seeding product need not be the same chemical substance as the end product of the continuous mass crystallization. However, it is advantageous if the seeding product has the same chemical composition as the end product. For example, crystals of ammonium sulfate are used for seeding during the continuous mass crystallization of ammonium sulfate.

The advantages of the invention lie

- in the defined control of the particle size distribution and, with that, of the average particle diameter of the end product,
- in the prevention of excessive cyclic fluctuations in the particle size distribution of the end product and, with that, in an improved utilization of the plant capacity,
- therein that the actual crystallization process has no effect on the control parameter (on the particle size of the seeding product) and
- that, during continuous seeding, the number of screen analyses for controlling the process can be decreased drastically.

Figure 1 shows a flow chart of the inventive, continuous, mass crystallization. A key for the symbols is given below:

1. crystallization apparatus (crystallizer)
2. pipeline (for feed solution)
3. pipeline (for vapors)
4. vapor compressor
5. heat exchanger
6. circulating pump
7. circulating pipeline
8. pipeline (for mash)
9. mash pump
10. centrifuge
11. interim storage tank
12. pump
13. pipeline (for mother liquor)
14. pipeline (for crystalline material)
15. pipeline (full partial flow)
16. elutriation crystallizer
17. centrifuge
18. pipeline (for crystalline material or part of the seeding product)
19. tank
20. pipeline for part of the seeding product
21. metering and conveying system
22. pipeline for seeding product

The crystallization is carried out in a continuous crystallization apparatus (1), preferably in an OSLO or a DRAFT TUBE BAFFLE (DTB) crystallizer.

The pre-heated feed solution (for example, with 37 $\pm$ 3 percent by weight of ammonium sulfate) is passed through pipeline (2) into the crystallizer.

The vapors arising are aspirated over pipeline (3) by a vapor compressor (4) and are compressed. The energy of the compressed vapors is transferred by means of heat exchangers (5) and a circulating pump (6) through the circulating pipeline (7) into the crystallization equipment.

Mash is withdrawn continuously through pipeline (8) and supplied with a mash pump (9) to a centrifuge (10). The mother liquor, which has been separated off, reaches an interim storage tank (11) and is transferred with the pump (12) over the pipeline (13) into the circulating pipeline (7). Over the pipeline (14), the crystalline material reaches the downstream processing plant.

A partial flow (liquid phase) is removed over pipeline (15) from the crystallization equipment and transferred to the elutriation crystallizer (16). The crystalline material, obtained here, is separated by a centrifuge (17) and added over pipeline (18) to the tank (19) as a possible component of the so-called seeding product.

A partial flow of the seeding product (for example, of ammonium sulfate crystals), which was produced, in relation to particle size distribution and amount by mechanical comminution of a partial amount of the end product, is also supplied to the tank (19) over the pipeline (20). From this, a pumpable suspension of crystals is produced and supplied, with the help of a metering and conveying system (21), over the pipeline (22) to the crystallizer in such a manner, that the crystals of the seeding product cannot settle.

The invention is described by the following examples, without being limited to these.

Example 1 (Comparison Example Without Additional Seeding Product)

In a continuously operating crystallization apparatus (DTB crystallizer), the active portion is about 280 m^3.

The preheated feed solution (ammonium sulfate solution, 38.5 ± 2% by weight ammonium sulfate content and a temperature of about 90°C) is supplied to the crystallizer without additional seeding product. The evaporation rate is 30T/H and the production rate is 20T/H (crystals withdrawn from the crystallizer). The solids content of the mash in the crystallizer is 35 to 40% by weight.

The particle size distribution, measured by means of the fraction greater than 1.8 mm over a period of 120 hours, is shown in Figure 2. The fluctuations in the particle size distributions are very large.

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Example 2 (discontinues addition of seeding product)

The basic operating state corresponds to that of Example 1, with the exception of the explicit requirement that, aside from the seeding product, all other materials supplied and recycled to the crystallization equipment must be absolutely free of solids.

By means of a particle size analysis of the crystalline particles from the interior of the crystallization equipment, a fraction is selected, the size range of which should be close to the average diameter of the particles of the seeding product.

The mass flow of seeding product is controlled discontinuously by means of defined upper and lower limiting values of this fraction, which can be determined empirically. The fraction greater than 0.4 mm and less than 1.0 mm of the crystalline material in the crystallization apparatus is used for the start and end of the discontinuous seeding. When this fraction falls below 1% by weight, the

crystallization apparatus is seeded. The solids portion of the seeding product is 10% by weight and the average particle diameter is about 0.6 mm..

When the fraction selected exceeds 2% by weight, seeding is suspended. If the upper limiting value is clearly exceeded, under some circumstances in conjunction with changes in other operating parameters, the specified parameter can be restored by supplying plant condensate to the crystallization apparatus.

The particle size distribution, measure by means of the fraction greater 1.8 mm over a period of 120 hours, is shown in Figure 3.

Example 3 (continues addition of seeding product)

The basic operating state corresponds to that of Example 1, however, with the explicit requirement that, aside from the seeding product, anything else, supplied to or recycled into the crystallization apparatus, must be absolutely free of solids.

The seeding product is supplied continuously to the crystallization equipment with fixed parameters, which are optimized empirically. The solids content of the seeding product is 7% by weight, based on the end product that is discharged and the average particle diameter is 0.6 mm. The seeding product is added continuously at the rate of 15 m^3/h.

Particle size analyses as a basis for controlling the operating state, are no longer required or can, at the very least, be reduced clearly in number. The particle size distribution, measured by means of the fraction of greater than 1.8 mm over a period of 120 hours, is shown in Figure 4.

<u>Example 4</u> (continues addition of seeding product)

The operating state corresponds to that of Example 3.

The seeding product is supplied continuously to the crystallization apparatus with fixed parameters, which are optimized empirically.

The solids content of the seeding product is 25% by weight, based on the discharged end product, and the average particle diameter is about 0.6 mm. The seeding product is metered in continuously at a rate of 25 m^3/h. The particle size is reduced selectively by an excess of seeding product.

The particle size distribution, measure by means of the fraction, greater than 1.8 mm over a period of 120 hours, is shown in Figure 5. In the period between the 24^{th} and the 80^{th} hour, the fraction greater than 1.8 mm is selectively moved into the 20% range by seeding.

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